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HYBRID KED/XRF MEASUREMENT OF MINOR ACTINIDES
IN REPROCESSING PLANTS

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INTRODUCTION

Minor actinides have received considerable attention recently in the nuclear power industry. Because of their potential value as recycle fuels in thermal and breeder reactors, reprocessing plants may have an economic incentive to extract Np, Am, and Cm from their waste streams.[1]

This report discusses the technique of hybrid densitometry and its potential to measure Np and Am in reprocessing plants. Precision estimates are made for the hybrid analysis of Np and Am in two types of dissolver solutions.

I. HYBRID SYSTEM

The hybrid system incorporates two solution assay techniques: k-edge absorption densitometry (KED) and x-ray fluorescence (XRF). A close-up view of the Los Alamos Hybrid Densitometer is shown in Figure 1. The basic components of the hybrid system are an x-ray generator, glass sample vial, and separate high-resolution detectors for KED and XRF. The sample itself may contain any number of actinides dissolved in nitric acid.
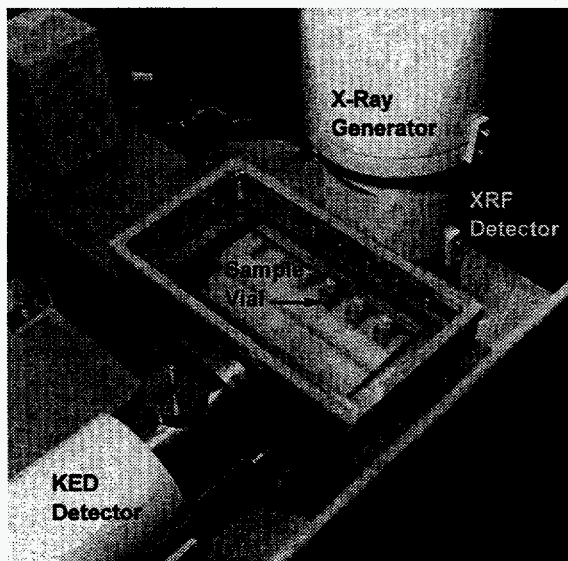
Figure 1. Close-up view of Los Alamos Hybrid Densitometer System.

The x-ray generator irradiates the sample with a filtered x-ray beam. The KED detector is positioned behind the sample, and measures the transmitted portion of the beam. +e XRF detector is positioned behind a long, narrow collimator that points toward the front of the sample vial. The angle between the incident beam and XRF collimator is 30 degrees. The XRF detector measures fluoresced x-rays that are emitted from the front portion of the solution.

In hybrid analysis, KED is used to determine the concentration of the major element, usually U or Pu. XRF is used to determine various ratios of concentrations, such as U/Pu, Pu/Am, and Pu/Np. Measured ratios are used to determine the ratio of each minor element to the major element. It is then a simple matter to calculate the concentrations of the minor elements. Hybrid analysis takes advantage of the strengths of the KED and XRF techniques.

II.   PROCESS FLOW

The process flow for a conventional reprocessing plant is illustrated in Figure 2. Spent fuel is placed in the fuel storage facility prior to reprocessing. In the first stage of reprocessing, fuel rods are chopped into small pieces. The resulting mixture is leached in nitric acid to form the dissolver solution. Most fission products and Am are removed in the first extraction cycle. Additional extraction steps are required to separate U and Pu from the remaining elements. Evaporation is performed to concentrate the U and Pu solutions, forming the product solutions.
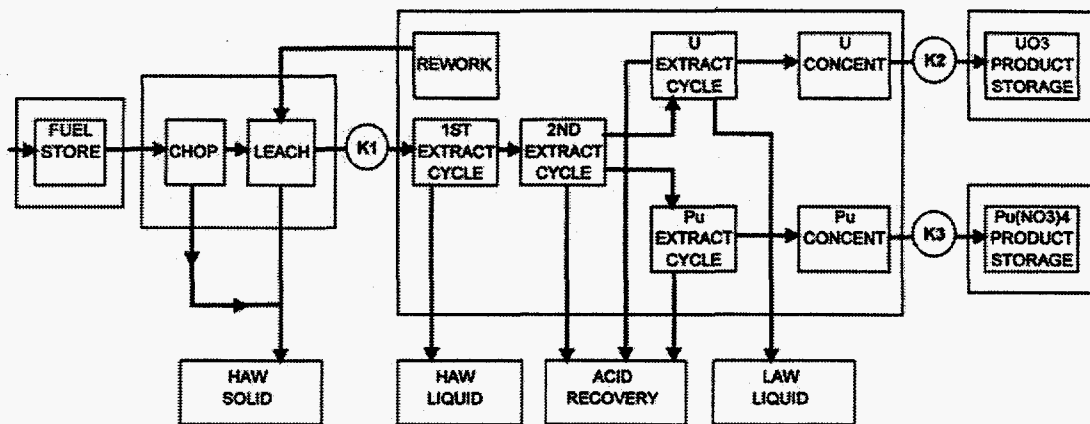

Figure 2. Process flow schematic for a conventional reprocessing plant. Key measurement points are labeled K1 through K3.

IAEA and Euratom have been using the hybrid KED/XRF technique to assay the dissolver solution samples, and KED to assay the U and Pu product solutions. The dissolver solution is monitored at key measurement point K1. The U and Pu product solutions are monitored at key measurement points K2 and K3, respectively. By measuring U and/or Pu concentrations at these three measurement points, it is possible to determine the material balance of U and Pu.

If a reprocessing plant extracted Am and Np, its process flow might resemble that of Figure 3. In this scenario, Am would be separated from the high-activity effluent of the first extraction cycle. Np would be separated from the effluent of the Pu extraction cycle. Evaporation steps would be performed to concentrate the Am and Np solutions. Such a plant would have four product solutions: U, Pu, Np, and Am.

As in the conventional reprocessing plant, the dissolver solution would be monitored at key measurement point K1. A hybrid KED/XRF densitometer would be used to measure the U, Pu, Np, and Am concentrations in the dissolver solution. The Np and Am product solutions are monitored at key measurement points K4 and K5, respectively. By measuring the Np and/or Am concentrations at these three measurement points, it would be possible to determine the material balance of Np and Am.
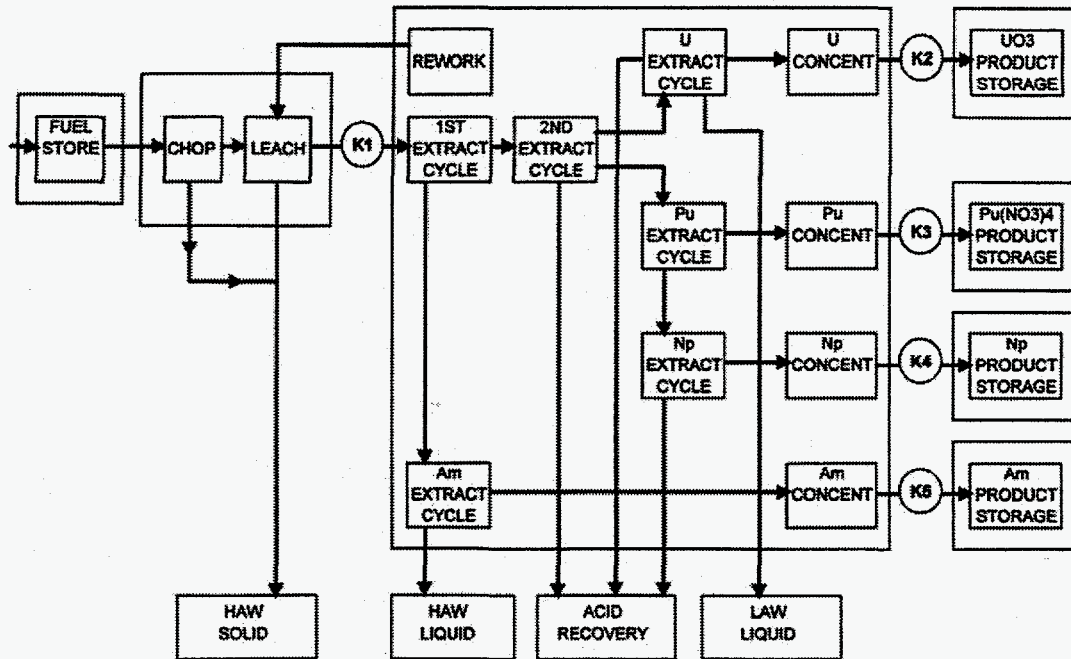
Figure 3. Process flow for a hypothetical reprocessing plant, showing separation of Np and Am. Key measurement points are labeled K1 through K5.

III. DISSOLVER SOLUTIONS

In this study, two types of dissolver solutions were considered. The first is from a fast breeder reactor (FBR) reprocessing plant; the other from a light water reactor (LWR) reprocessing plant. These solutions are characterized in Table 1.

Table 1. Comparison of FBR and LWR Dissolver Solutions.

	FBR Dissolver	LWR Dissolver
U Concentration (g/l)	200	200
Pu Concentration (g/l)	50	2
Pu/Np Ratio	10	30
Pu/Am Ratio	10	30

We have developed computer codes that simulate the performance of the hybrid system.[2,3] These codes generate KED and XRF spectra that correspond to a given solution. Simulated spectra for the FBR and LWR dissolver solutions are illustrated below. All simulated spectra in this study correspond to a live time of 1000 seconds.

Figure 4 shows the KED reference spectrum and simulated KED spectra for FBR and LWR dissolver solutions. The K absorption edge of uranium (at 115.606 keV) is clearly visible in both the FBR and LWR spectra. The K absorption edge of Pu (at 121.797 keV) is prominent in the FBR spectrum, but not in the LWR spectrum.
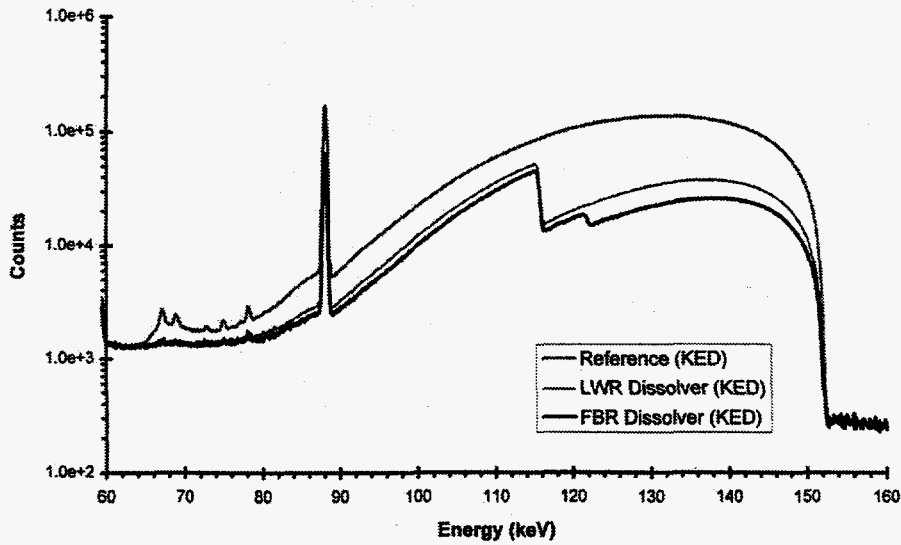
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Figure 4. Simulated KED Spectra for FBR and LWR Dissolver Solutions. Reference spectrum is uppermost trace in graph.

The differences between the FBR and LWR spectra are more readily observed if the spectra are plotted in LnLn(1/Transmission) versus Ln(Energy) space. Because of the energy dependence of mass attenuation coefficients, we expect measured data to be linear on either side of each absorption edge in LnLn(1/T) vs. Ln(Energy) space. This can be seen in Figure 5. Single element KED analysis is performed by doing a linear fit in this space, using regions above and below the edge. The concentration of the element is calculated using the results of the linear fitting.

In Figure 5, the U and Pu edges are prominent for the FBR dissolver solution. Very small Np and Am edges can also be observed in the FBR data. In the LWR data, a Pu edge can hardly be spotted, and the Np and Am edges are unidentifiable.
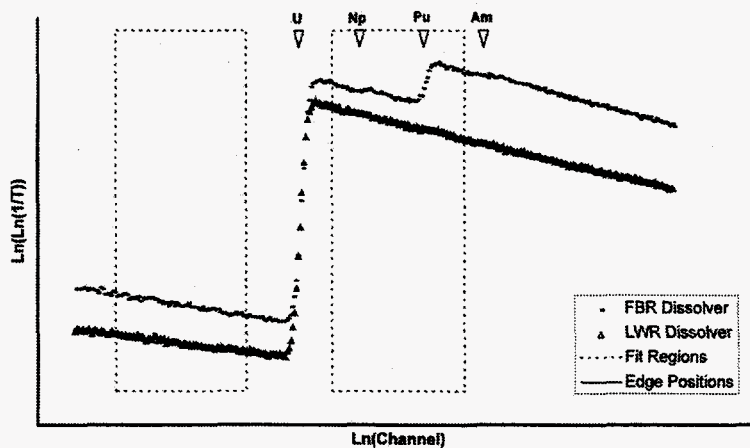

Figure 5. Simulated KED spectra for FBR and LWR dissolver solutions, plotted in LnLn(1/T) vs Ln(Energy) space. Positions of absorption edges are marked.

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Figure 6 shows the XRF reference spectrum and simulated XRF spectra for FBR and LWR dissolver solutions. For each element present in a simulated solution, 10 x-ray peaks are generated. These include the $K_{\alpha 1}$, $K_{\alpha 2}$, and $K_{\alpha 3}$ peaks, and various K_β peaks. Several of the 40 x-ray peaks simulated in the dissolver solutions can be observed in Figure 6. The K_α peaks are seen below 108 keV and the K_β peaks are found above 110 keV.
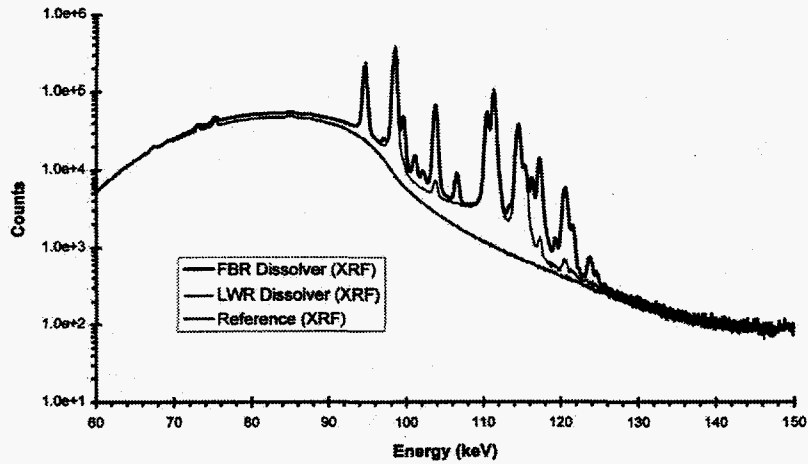
Figure 6. Simulated XRF spectra for FBR and LWR dissolver solutions. Reference spectrum is lowest trace on graph.

The K_α peaks are of primary interest in XRF analysis. Figure 7 compares the simulated FBR and LWR spectra, shown with the reference spectrum subtracted. The range of energies was narrowed to feature the K_α peaks of U, Np, Pu, and Am. Note that the uranium K_α peaks of the FBR spectrum are slightly smaller than those of the LWR spectrum. This is due to attenuation effects within the FBR dissolver solution, which contains more Pu, Np, and Am.

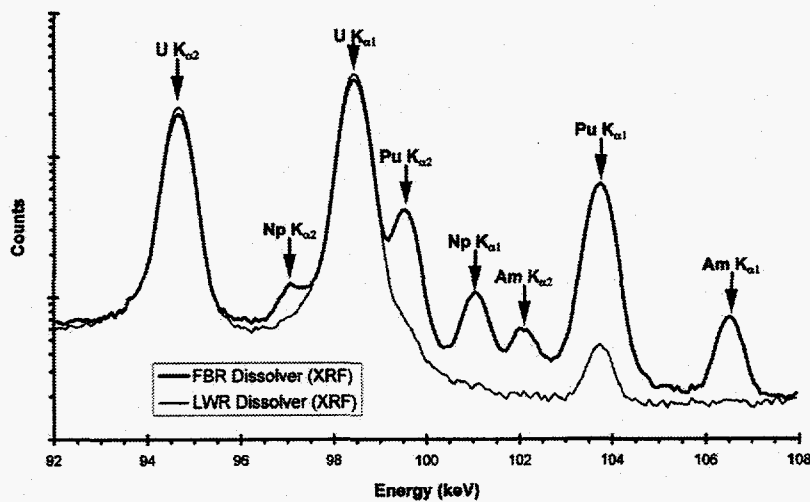*Figure 7. Comparison of XRF Spectra for FBR and LWR Dissolver solutions. Reference spectrum was subtracted from both series.*

The Pu K_α peaks in the FBR spectrum have a significantly greater area than those in the LWR spectrum because there is much more Pu to fluoresce in the FBR dissolver solution. Similar observations can be made regarding the K_α peaks of Np and Am. In the LWR dissolver solution spectrum, the K_α x-rays of Np and Am cannot be distinguished from noise.

IV.   ESTIMATED PRECISION

Hybrid analysis was performed on the simulated FBR and LWR dissolver solution spectra. First, the XRF spectra were analyzed to determine the percent uncertainties in the U/Pu, Pu/Np, and Pu/Am ratios. Then the KED spectra were analyzed to determine the percent uncertainty in the concentration of the major element.

In KED analysis, the fixed ratio technique was used.[4] This technique utilizes U/Pu, Pu/Np, and Pu/Am ratios to mathematically strip out the attenuation effects of minor elements in the solution. Single-element KED analysis is performed on the deattenuated spectrum to determine the concentration of the major element in the solution. In this study, the actual ratios known from simulation were used in the fixed-ratio technique.

Hybrid results for FBR and LWR dissolver solutions are shown below in Table 2. Uranium was the major element in KED analysis for both dissolver solutions.

Table 2. Estimated Hybrid Precision for FBR and
LWR Dissolver Solutions.

	FBR Dissolver	LWR Dissolver
KED σ(U)	0.2%	0.2%
XRF σ(U/Pu)	0.2%	1.4%
XRF σ(Pu/Np)	0.8%	N/A
XRF σ(Pu/Am)	0.9%	N/A

With the FBR dissolver solution, the x-ray peaks of Np and Am were readily identified and measured by the XRF analysis code. No sample preparation is needed for the FBR dissolver solution.

The situation is different for the LWR dissolver solution. Recall that in Figure 7, the K_α peaks of Np and Am in the LWR spectrum were indistinguishable from noise. This was verified by the XRF analysis code, which did not detect the presence of Np or Am in the LWR dissolver solution. We therefore cannot expect to measure Np or Am in the straight LWR dissolver solution using the Hybrid technique.

In order for the hybrid system to measure Np and Am at key measurement point K1 in the LWR reprocessing plant, some preparation of the dissolver solution sample would be required. This would involve chemical separation to remove most of the uranium from the dissolver solution. Evaporation would also be needed to concentrate the remaining liquid severalfold. In this study, three preparation scenarios were considered for the LWR dissolver solution. These are detailed in Table 3 below.

Table 3. Possible Preparations of LWR Dissolver Solution.

	Solution 1	Solution 2	Solution 3
Separation Quality	Fair	Good	Excellent
U Removal	97.0%	99.0%	99.9%
Evaporation factor	20	20	50
Known U (g/l)	120	40	10
Known Pu (g/l)	40	40	100

Simulated KED and XRF spectra were generated for the above solutions. Hybrid analysis, as described earlier, was performed on the simulated spectra. The major element in KED analysis was U for solution 1 and Pu for solutions 2 and 3. The results for the prepared LWR solutions are shown in Table 4.

Table 4. Estimated Hybrid Precision for Prepared LWR Solutions.

	Solution 1	Solution 2	Solution 3
KED $\sigma(U)$	0.2%	---	---
KED $\sigma(Pu)$	---	0.5%	0.2%
XRF $\sigma(U/Pu)$	0.2%	0.3%	0.4%
XRF $\sigma(Pu/Np)$	2.3%	2.1%	1.0%
XRF $\sigma(Pu/Am)$	2.4%	2.2%	1.1%

V.   CONCLUSIONS

Hybrid KED/XRF densitometer systems now in operation at reprocessing plants have the potential to measure Np and Am, in addition to U and Pu. No hardware alterations would be required in these systems. However, the analysis software would need to be upgraded. New hybrid analysis techniques for measuring Np and Am would be incorporated.

At an FBR reprocessing plant, Np and Am could be measured in dissolver solution samples with no sample preparation. The estimated precision for a 1000-s assay is 0.8% for Np and 0.9% for Am.

At an LWR reprocessing plant, dissolver solution samples would require some preparation. This preparation would involve partial U separation (97% to 99.9% removal), and evaporation (20 to 50 fold concentration). The estimated precision for a 1000 s assay ranges from 1.0% to 2.3% for Np and from 1.1% to 2.4% for Am. The precision depends upon the extent of sample preparation.

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2.   M. L. Collins and S.-T. Hsue, "Simulation of X-Ray Fluorescence Spectra," Los Alamos National Laboratory report LA-UR-96-2603 (to be published in 37th Annual *Nuclear Materials Management*, Proceeding Issue).

3.   S.-T. Hsue and M. L. Collins, "Simulation of Absorption Edge Densitometry." Los Alamos National Laboratory report LA-12874-MS (November 1994).

4.   S.-T. Hsue and M. L. Collins, "New Analysis Technique for K-Edge Densitometry Spectra." Los Alamos National Laboratory report LA-UR-95-3222. Proceedings of the Fifth International Conference on Facility Operations—Safeguards Interface, American Nuclear Society, Jackson Hole, Wyoming, September 1995.